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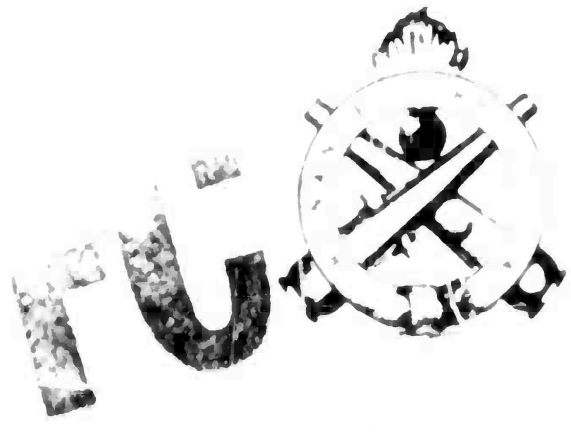

ABERDEEN PROVING GROUND
MARYLAND

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CONTENTS

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Report No. CCL 62

Copy No.

LOW SURFACTANT CONTENT AMPHOTERIC CLEANERS

by

A. Mankowich

13 August 1958

OCO, R&D Branch Project No.
TB4-006A
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Coating and Chemical Laboratory
Aberdeen Proving Ground
Maryland

UNCLASSIFIED

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ABSTRACT

Low surfactant content alkaline cleaners have been developed suitable for use with missile component parts of magnesium, aluminum, zinc, etc. These compounds possess excellent detersive, heat stability and cleaning capacity characteristics and economy. They contain only 3.0 percent of a specific quaternary imidazolium hydroxide amphoteric surfactant plus 1.5 percent isooctylphenyl nonaethylene glycol ether (IOPNG). The amphoteric agent is the dicarboxylic analogue of the coconut oil derivative. Nonionics of the alkyl polyethylene glycol ether or alkyl polyethylene glycol thioether types may be substituted for IOPNG. The developed compounds permit a saving of about 16 percent over present-type Specification P-C-436a products.

I INTRODUCTION

Initial studies of alkaline cleaners in this Laboratory led to the promulgation on 23 June 1954 of Federal Specification P-C-436a, "Cleaning Compound, Alkali Type". This specification covered one class of cleaning dompound suitable for use in the hot soak tank cleaning of both ferrous and missile component (nonferrous) parts. Products conforming to this specification were suitable for use with magnesium, aluminum and die-cast zinc alloys because of their metasilicate inhibitor content and medium pH requirement (12.1 maximum at 25°C in 7.5 percent by weight solution). These medium pH cleaning compounds exceeded the conventional, heavy duty (high alkalinity) ferrous cleaners in detersive ability because they contained a specific synergistic surfactant combination. We have postulated that a cleaner capable of passing the cleaning efficiency test of the specification is possessed of an "improved detergency", surpassing that of the conventional cleaner. We have found that "improved detergency" depends on the simultaneous possession by the cleaner of very high hydrophile strength and a certain degree of lipophile strength, as evidenced by the ability to remove asphalt and mineral oil soils respectively.

Further studies of alkaline cleaners in this Laboratory (1,2,) have included investigations of compounds containing polyoxyalkylene diol nonionic agents and amphoteric surfactants of the quaternary imidazolium hydroxide type. Developed compositions containing either type of surface-active agent, and possessing the "improved detergency" characteristic of Specification P-C-436a products, provided ideal soak-type, alkaline cleaners of missile component parts.

Since the first report on compounds containing amphoteric surfactants was submitted, additional types of the latter have become available. This investigation covers further research and development of alkaline cleaners containing amphoteric additives.

II DETAILS OF TEST

A. Test Methods

The test methods used in this investigation were those given in Federal Specification P-C-436a, with the exception that the concentration of the cleaning solutions was varied from 7.5 to 8.0 percent as noted, instead of using the specified 7.5 percent.

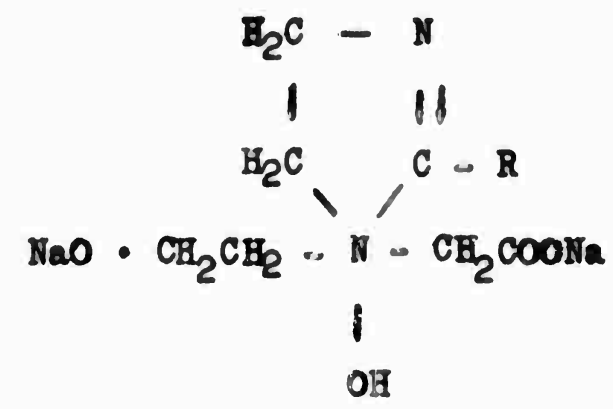
1. Surfactants

The amphoteric surfactants (45% active content) used in the original investigation are the following:

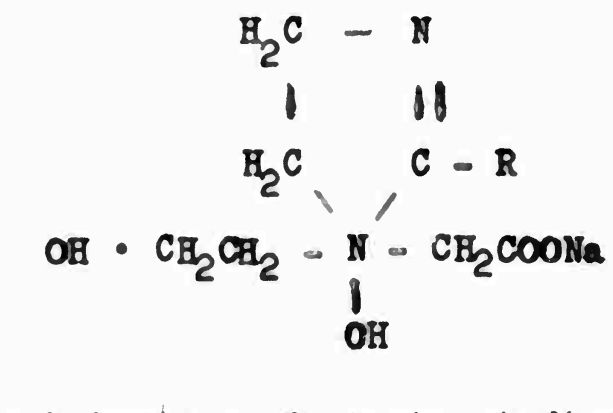
Surfactant	Derivative	R
1	Capric acid	C_9H_{19}
2	Lauric acid	$C_{11}H_{23}$
3	Coconut oil	R_1
4	Myristic acid	$C_{13}H_{27}$

Surfactant	Derivative	R
5	Stearic acid	$C_{17}H_{35}$

General formula for surfactants 2, 3 and 4 was:



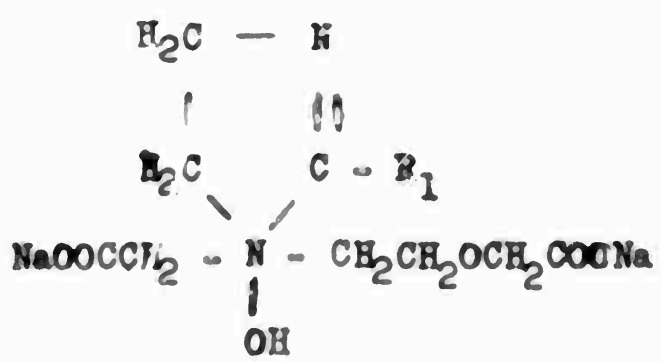
General formula for surfactants 1 and 5 was:



The new amphoteric surfactants studied herein were:

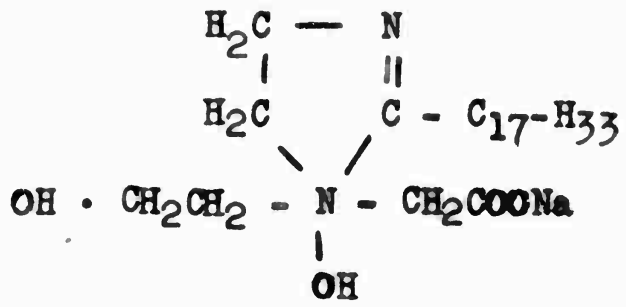
No. 6 - A salt-free modification of No. 3, a cocoanut oil derivative.

No. 7 - A 49% active, dicarboxylic analogue of No. 3, with the following formula:



No. 8 - A salt-free modification of No. 7

No. 9 - A 35% active salt-free, oleic acid derivative with the following formula:



B. Results

1. No. 7 and No. 8 Amphoteric - Nonionic Cleaners (Tables I, II, III)

Alkaline cleaners containing 3.0 to 14 percent of the No. 7 or No. 8 amphoteric surfactants, the dicarboxylic analogues of the cocoonut oil derivative (No. 3), plus 1.5 percent of the nonionic isooctylphenyl nonaethylene glycol ether (ICPNG) possessed good asphalt detergency. Increasing the ICPNG content to 6.0 percent narrowed the No. 7 amphoteric range for satisfactory asphalt removal to 7.5 to 14 percent and the No. 8 amphoteric (salt-free modification) range to 6.0 to 14 percent. Substitution of t-dodecyl nonaethylent glycol thioether or tridecyl dodecaethoylene glycol ether for ICPNG in the economically-important formulations containing 3.0 percent of the No. 7 of No. 8 amphoteric plus 1.5 percent of nonionic additive gave products that had good asphalt detergency also (Table III). Lauric diethanolaride was not a satisfactory additive in the latter application.

2. No. 3 and No. 6 Amphoteric - Nonionic Cleaners (Tables IV, V)

In the first investigation of amphoteric surfactants (3), it was found that cleaners containing 3.0 to 9.8 percent IOPNG with 14 percent of the coconut derivative, amphoteric No. 3, were good asphalt strippers, and that reducing the latter to 9.0 to 11.7 percent in compounds containing 5.8 to 6.0 percent ICPNG resulted in the loss of asphalt detergency (original data given in Table V). Replacing the No. 3 amphoteric by its salt-free modification, No. 6, in compounds containing 9.0 to 11.7 percent of the latter plus 5.8 to 6.0 percent ICPNG resulted in good asphalt detergency (Table IV). In a cleaner containing 14 percent amphoteric No. 6, the IOPNG content could not be decreased below 3.0 percent for satisfactory asphalt removal, thus paralleling results with amphoteric No. 3. The undecyl derivative, No. 2, showed a slight superiority over the salt-free No. 6 amphoteric, satisfactory asphalt removal being provided by a compound containing 14 percent of the latter with only 2.0 percent ICPNG (Table V).

3. Amphoteric - Anionic Cleaners (Table VI)

Cleaning compounds containing 9.0 to 14 percent of the No. 6 or No. 7 amphoteric surfactants plus 6.0 percent of sodium dodecyl benzene sulphonate, SDBS, were unsatisfactory asphalt strippers, as was also a compound containing 3.0 percent amphoteric No. 8 and 1.5 percent SDBS.

4. No. 9 Amphoteric Cleaners (Table VII)

Cleaners containing 11.7 to 14.1 percent of the No. 9 amphoteric, the salt-free oleic acid derivative, plus 5.7 percent IOPNG were able to strip asphalt. Reduction of the No. 9 content to 9 percent caused the cleaner to

lose its asphalt detergency. A cleaner containing 14.1 percent of the No. 5 amphoteric, a stearic acid derivative, with 5.7 percent IOPNG has no asphalt detergency.

5. Cleaning Capacity (Table VIII)

The economically-important formulation containing 3.0 percent of the No. 8 amphoteric plus 1.5 percent of IOPNG exhibited considerable cleaning capacity by cleaning seventeen consecutive asphalt-soiled test panels in the same 1,600 cc batch of cleaner.

6. Stability Tests (Table IX)

Several cleaners containing the No. 8 amphoteric, the salt-free dicarboxylic analogue of the coconut oil derivative, passed the stability test of Fed. Spec. P-C-436a; that is, they possessed satisfactory mineral oil and asphalt detergency subsequent to 40 hours of boiling. Included was the low surfactant-content formulation containing 3.0 percent of the No. 8 amphoteric plus 1.5 percent IOPNG.

7. Miscellaneous Tests (Table X)

Low surfactant-content cleaners containing the No. 7 and No. 8 amphoterics passed the aluminum corrosion and pH tests of Spec. P-C-436a, but failed the surface tension requirement.

8. Discussion of Results

The development of alkaline cleaners possessing "improved detergency", suitable for use on missile component parts, and containing a surfactant content of only 4.5 percent (3.0 percent of amphoteric No. 7 or No. 8 plus 1.5 percent of IOPNG), is of considerable importance. The Standard Comparison Cleaning Compound of Fed. Spec. P-C-436a contains a total surfactant content of 20 percent or a net active content of 11.1 percent. Based on current market quotations, the developed low surfactant content cleaning compounds permit a saving of approximately 16 percent, the cost of the surfactant content being reduced about 50 percent.

Although possessing excellent cleaning capacity and heat stability characteristics, the developed low surfactant content-amphoteric cleaners failed to meet the surface tension requirement of Spec. P-C-436a. The surfactant ingredients had good surface tension depressant properties, but low surfactant content resulted in high surface tension. These amphoteric cleaners differed from the polyoxyalkylene diol cleaners developed at this Laboratory (1) and the one proposed by a supplier (1) in that the surfactant ingredients of the latter products were poor surface tension depressants.

From the standpoint of detersive ability, amphoterics No. 7 and No. 8, dicarboxylic analogues of the coconut oil derivative, proved to be superior to all other quaternary imidazolium hydroxide surfactants studied, with No. 8, the salt-free modification of No. 7, slightly the better of the two. These were followed, in order of their detersive effectiveness, by amphoterics No. 2 (lauric acid derivative), No. 6 (salt-free modification of the coconut oil derivative, No. 3) and No. 3. This comparison was made on the

basis of cleaners containing the amphoteric surfactants in combination with IOPNG, a nonionic of the alkylaryl polyethylene glycol ether class. Limited tests with nonionics of the alkyl polyethylene glycol ether and alkyl polyethylene glycol thioether types indicated they were satisfactory substitutes for IOPNG.

In view of their excellent detersive ability, economy and suitability for use with missile component parts, it is intended to have the developed low-surfactant content amphoteric cleaners field tested by the K-Group, National Maintenance Point, Raritan Arsenal, Metuchen, N. J. Satisfactory field tests will be followed by a proposed revision of Fed. Spec. P-C-436a, which will be rewritten around the amphoteric cleaner as the Standard Comparison Cleaning Compound.

III REFERENCES

1. Engineering Laboratories Report No. 7, August 1955

2. Engineering Laboratories Report No. 39, April 1956

3. Coating and Chemical Laboratory Report No. 34, November 1957

APPENDIX

TABLES I - X

TABLE I

No. 7 Amphoteric - Alkyl Aryl Polyethylene Glycol Ether Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
7	8.0	41.7	14.6	40.2	2.0	1.5	poor
"	8.0	41.2	14.5	39.8	3.0	1.5	good
"	8.0	40.8	14.3	39.4	4.0	1.5	good
"	8.0	39.1	13.6	37.8	8.0	1.5	good
"	8.0	36.4	12.7	35.4	14.0	1.5	good
"	7.5	37.8	13.2	37.0	6.0	6.0	poor
"	7.5	37.3	13.0	36.2	7.5	6.0	good
"	7.5	36.7	12.8	35.5	9.0	6.0	good
"	8.0	34.6	12.1	33.5	14.1	5.7	good

* isooctylphenyl nonaethylene glycol ether

TABLE II

No. 8 Amphoteric - Alkyl Aryl Polyethylene Glycol Ether Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
8	8.0	41.7	14.6	40.2	2.0	1.5	poor
"	8.0	41.2	14.5	39.8	3.0	1.5	good
"	8.0	40.8	14.3	39.4	4.0	1.5	good
"	8.0	39.9	13.9	38.7	6.0	1.5	good
"	8.0	39.1	13.6	37.8	8.0	1.5	good
"	8.0	38.1	13.3	37.1	10.0	1.5	good
"	8.0	36.4	12.7	35.4	14.0	1.5	good
"	8.0	39.0	13.4	37.6	4.0	6.0	poor
"	7.5	37.8	13.2	37.0	6.0	6.0	good
"	7.5	37.3	13.0	36.2	7.5	6.0	good
"	8.0	34.6	12.1	33.5	14.1	5.7	good

* isooctylphenyl nonaethylene glycol ether

TABLE III

No. 7 and No. 8 Amphoteric - Miscellaneous Nonionic Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive	
7	8.0	41.2	14.5	39.8	3.0	1.5*	good
8	8.0	41.2	14.5	39.8	3.0	1.5*	good
8	8.0	41.2	14.5	39.8	3.0	1.5▲	good
8	8.0	41.2	14.5	39.8	3.0	1.5°	poor

* - tridecyl dodecaethylene glycol ether

▲ - t-dodecyl nonaethylene glycol thioether

o - lauric diethanolamide

TABLE IV

No. 6 Amphoteric - Alkyl Aryl Polyethylene Glycol Ether Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
6	8.0	36.4	12.7	35.4	14.0	1.5	poor
"	8.0	36.2	12.6	35.2	14.0	2.0	poor
"	8.0	35.8	12.5	34.7	14.0	3.0	good
"	8.0	40.6	14.1	39.3	3.0	3.0	poor
"	7.5	37.3	13.0	36.2	7.5	6.0	poor
"	7.5	36.7	12.8	35.5	9.0	6.0	good
"	7.7	35.6	12.4	34.5	11.7	5.8	good

* isooctylphenyl nonaethylene glycol ether

TABLE V

No. 2 and No. 3 Amphoterics - Alkyl Aryl Polyethylene Glycol Ether Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
2	8.0	36.4	12.7	35.4	14.0	1.5	poor
"	8.0	40.2	13.9	37.9	6.0	2.0	good
"	8.0	36.2	12.6	35.2	14.0	2.0	good
"	7.5	37.3	13.0	36.2	7.5	6.0	poor
"	7.5	36.7	12.8	35.5	9.0	6.0	good
"	8.0	34.6	12.1	33.5	14.1	5.7	good
3	8.0	39.7	13.7	37.6	6.0	3.0	poor
"	8.0	35.8	12.5	34.7	14.0	3.0	good
"	7.5	36.7	12.8	35.5	9.0	6.0	poor
"	7.7	35.6	12.4	34.5	11.7	5.8	poor
"	8.0	34.6	12.1	33.5	14.1	5.7	good

* isooctylphenyl nonaethylene glycol ether

TABLE VI

No. 6, 7 and 8 Amphoteric - Anionic Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
6	8.0	34.5	12.0	33.5	14.0	6.0	poor
6	7.5	36.7	12.8	35.5	9.0	6.0	poor
7	8.0	34.5	12.0	33.5	14.0	6.0	poor
7	7.5	36.7	12.8	35.5	9.0	6.0	poor
8	8.0	41.2	14.5	39.8	3.0	1.5	poor

* Sodium dodecyl benzene sulphonate

TABLE VII

No. 9 and No. 5 Amphoteric Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	Additive*	
9	8.0	34.6	12.1	33.5	14.1	5.7	border-line
9	7.7	35.6	12.4	34.5	11.7	5.8	good
9	7.5	36.7	12.8	35.5	9.0	6.0	poor
5	8.0	34.6	12.1	33.5	14.1	5.7	poor

* isooctylphenyl nonaethylene glycol ether

TABLE VIII

Cleaning Capacity - Low Percentage Amphoteric No. 8 Cleaner

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					Asphalt Detergency
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	IOPNG	
8	8.0	41.2	14.5	39.8	3.0	1.5	*

* - 17 consecutive asphalt-soiled test panels were cleaned satisfactorily in the same 1,600 cc batch of cleaner according to Spec. P-C-436a procedures.

TABLE IX

Spec. P-C-436a Stability Tests - Amphoteric Cleaners

Amphoteric Surfactant	% Solution, grams/100 cc	Cleaner Composition - % By Weight					P-C-436a Stability Test
		$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	IOPNG	
8	8.0	36.4	12.7	35.4	14.0	1.5	passes
8	8.0	40.8	14.3	39.4	4.0	1.5	passes
8	8.0	41.2	14.5	39.8	3.0	1.5	passes

TABLE X

Miscellaneous Tests - Amphoteric Cleaners

Amphoteric Surfactant	Cleaner Composition - % By Weight					Spec. P-C-436a Tests
	$Na_2SiO_3 \cdot 5H_2O$	$NaH_2PO_4 \cdot H_2O$	$Na_3PO_4 \cdot 12H_2O$	Amphoteric	IOPNG	
8	41.2	14.5	39.8	3.0	1.5	Aluminum corrosion - passes pH = 12.0 - passes
7	41.2	14.5	39.8	3.0	1.5	Surface tension = 39.5 dynes/cm - fails

DEPARTMENT OF THE ARMY
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
3071 ABERDEEN BOULEVARD
ABERDEEN PROVING GROUND, MARYLAND 21005-5201

REPLY TO
ATTENTION OF

05 NOV 2012

RDCB-DPC-RS

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (ECBC) (RDCB-D), 5183 Blackhawk Road, Aberdeen Proving Ground, MD 21010-5424

FOR Office of the Chief Counsel, US Army Research, Development and Engineering Command (RDECOM) (AMSRD-CCF/Ms. Kelly Knapp), 3071 Aberdeen Boulevard, Aberdeen Proving Ground, MD 21005-5424

SUBJECT: Operations Security/Freedom of Information Act (FOIA) Review Request

1. The purpose of this memorandum is to recommend the release of information in regard to RDECOM FOIA Request, FA-13-0001.

2. On 2 October 2012, the Edgewood Chemical Biological Center (ECBC) received RDECOM FOIA Tasker #FA-13-0001. The request originated from the Defense Technical Information Center (DTIC) at Fort Belvoir, VA.

3. The following documents were reviewed by Subject Matter Experts from ECBC and deemed appropriate for both downgrade and release:

a. AD 149572, Amphoteric Surfactants in Alkaline Cleaners, 30 Oct 57.

b. AD 206020, Low Surfactant Content Amphoteric Cleaners, 13 Aug 1958.

c. AD 249437, Amino Carbolic Amphoteric Surfactants in Alkaline Cleaners, 9 Nov 1960.

4. The ECBC point of contact for this action is Mr. Ronald L. Stafford, 410-436-6810 or ronald.l.stafford.civ@mail.mil.

JUNE K. SELLERS
Security Manager